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**QUANTUM WELL THERMOELECTRICS FOR CONVERTING WASTE HEAT TO
ELECTRICITY**

QUARTERLY TECHNICAL PROGRESS REPORT

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Submitted By

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ABSTRACT

New thermoelectric materials using Quantum Well (QW) technology are expected to increase the energy conversion efficiency to more than 25% from the present 5%, which will allow for the low cost conversion of waste heat into electricity.

Hi-Z Technology, Inc. has been developing QW technology over the past six years. It will use Caterpillar, Inc., a leader in the manufacture of large scale industrial equipment, for verification and life testing of the QW films and modules.

Other members of the team are Pacific Northwest National Laboratory, who will sputter large area QW films. The Scope of Work is to develop QW materials from their present proof-of-principle technology status to a pre-production level over a proposed three year period. This work will entail fabricating the QW films through a sputtering process of 50 μm thick multi layered films and depositing them on 12 inch diameter, 5 μm thick Si substrates.

The goal in this project is to produce the technology for fabricating a basic 10-20 watt module that can be used to build up any size generator such as: a 5-10 kW Auxiliary Power Unit (APU), a multi kW Waste Heat Recovery Generator (WHRG) for a class 8 truck or as small as a 10-20 watt unit that would fit on a daily used wood fired stove and allow some of the estimated 2-3 billion people on earth, who have no electricity, to recharge batteries (such as a cell phone) or directly power radios, TVs, computers and other low powered devices.

In this quarter Hi-Z has continued fabrication of the QW films and also continued development of joining techniques for fabricating the N and P legs into a couple. The upper operating temperature limit for these films is unknown and will be determined via the isothermal aging studies that are in progress. We are reporting on these studies in this report. The properties of the QW films that are being evaluated are Seebeck, thermal conductivity and thermal-to-electricity conversion efficiency.

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2 INTRODUCTION

Fabrication development of high efficiency quantum well (QW) thermoelectric continues with the P and N-type Si/SiGe films on Kapton and Si substrate.

Gradient life testing are underway. One couple has achieved about 4500 hours at T_H of 300°C and T_C of 50°C with some degradation which we will investigate in the future. Emphasis is now shifting towards couple and module design and fabrication. Preliminary design calculations regarding the development of actual quantum well modules will be presented for both power prediction and cooling applications. These modules can be used in future energy conversion system as well as air conditioning system designs (Ref. 1-8). The large sputtering system at Hi-Z is coming on line for large sample fabrication needed for this task. This AJA sputtering machine is shown in Figure 1 on the next page.

3 QUANTUM WELL FILM GROWTH IN LARGE SPUTTERING MACHINE

The AJA sputtering machine has been calibrated to determine the operating parameters of the machine for creating ideal quantum well samples. The major improvements were on the heaters and more automated programmed film layer operation. The heater problem seemed to have stemmed from poor insulation techniques used on the heater bulb wiring and the close proximity of the leads on the Conflat connectors. Both of these problems were fixed by applying Glyptol insulating varnish to the Conflat connectors and wrapping the leads with Kapton tape. The area behind the heater shields where the leads pass through also appeared to have plasma shorting and this was covered with Kapton tape as a preventative measure and AJA is working on the software issues. We were able to do simple runs in the manual mode and were able to develop some good samples. Figure 2, shows a Scanning Electron Microscope view of a sample's cross section. This sample is pure Silicon sputtered at the rate of 720 Angstroms/minute. The layer thickness was nominally 1.56 µm. This held true over the entire width of the sample.



Figure 1. Hi-Z new sputtering 34" diameter chamber processes up to (6) 8" wafers, (9) 6" wafers or hundreds of small substrates with up to 2 different materials. The system is fitted with 400/C backside quartz lamp heating, MagLev turbo and a dry pump.

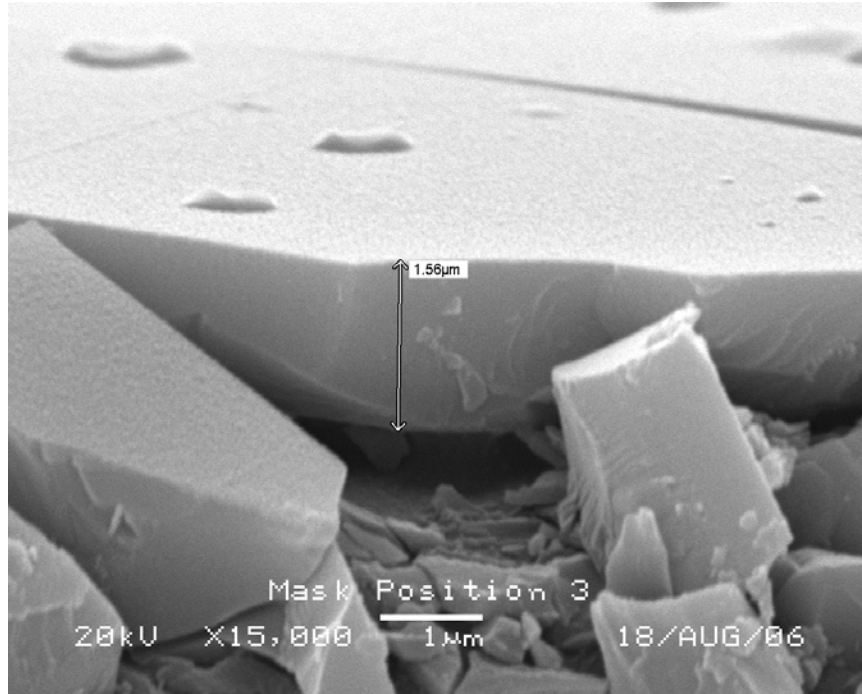


Figure 2. Si buffer on Kapton for quantum well films show uniform deposition thickness at 720 Å/minute over 6 inch samples sputter diameter. SEM of Si on Kapton shows good foundation for quantum well films.

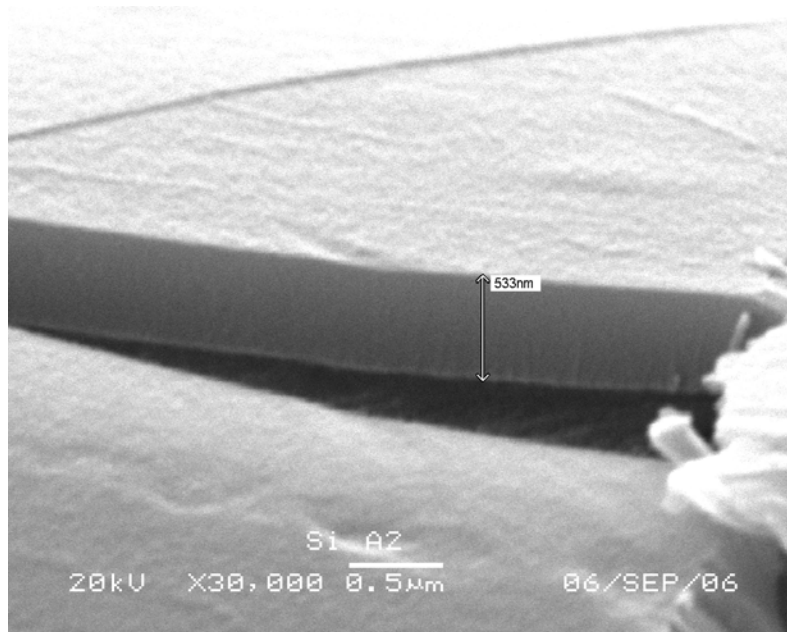


Figure 3. SEM of Silicon buffer layer on Kapton deposited at 485 Angstroms/minute. Again, across the entire sample, there was very good uniformity at approximately 0.5 μm.

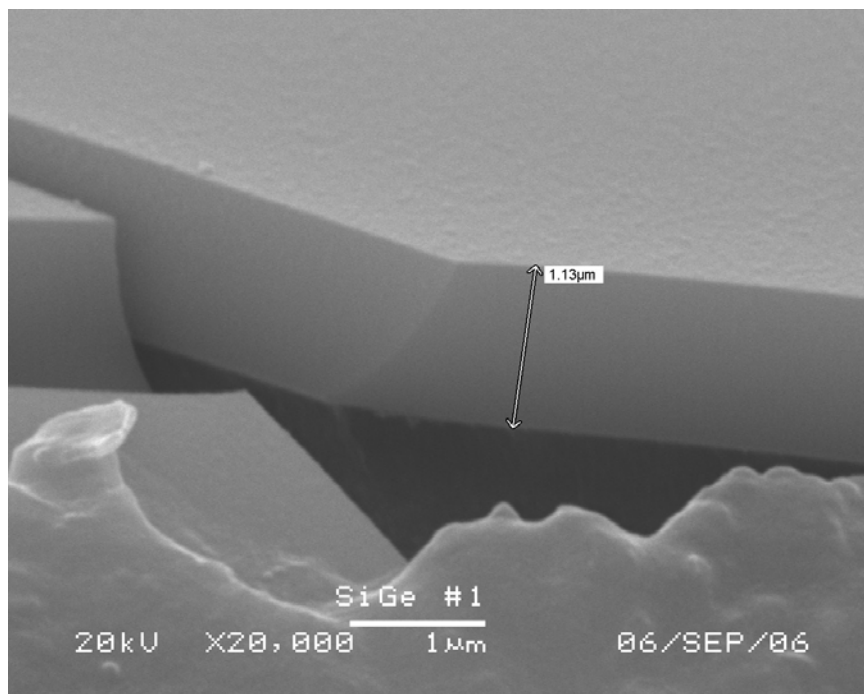
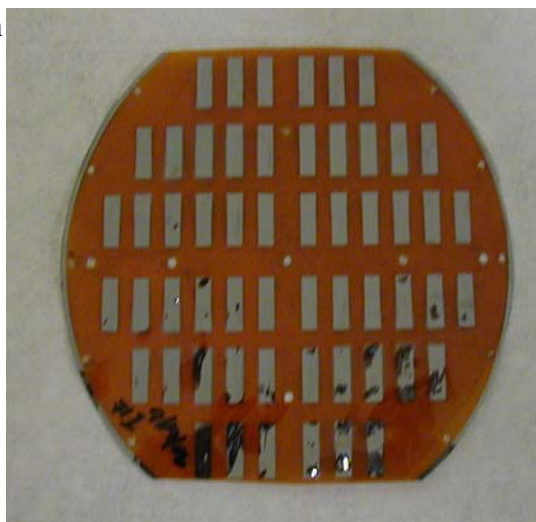


Figure 4. SEM of Silicon Germanium quantum well sample laid down at a rate $720 \text{ \AA}/\text{minute}$ but at half the total time as the Silicon in Figure 1.

The target deposition rate is $100 \text{ Angstroms}/\text{minute}$, and from the data that has been gathered, machine modifications are in progress to achieve this. They are:

1. Modify the drive train to increase the dwell time the samples are presented to the targets. This is in process at this time and was completed by the end of September 2006.
2. Re-calibrate the temperature profile to allow for the increased dwell. This is expected to be completed within 3 days of the speed modifications.

Figure 5. Quantum well sample film with a $0.2 \mu\text{m}$ Si base then alternating 100 Angstrom layers of Si and Si/Ge for a total of $2 \mu\text{m}$. At this time a Scanning Electron Microscope of the cross section is not available. This sample was run at a rate of $200 \text{ Angstroms}/\text{minute}$.



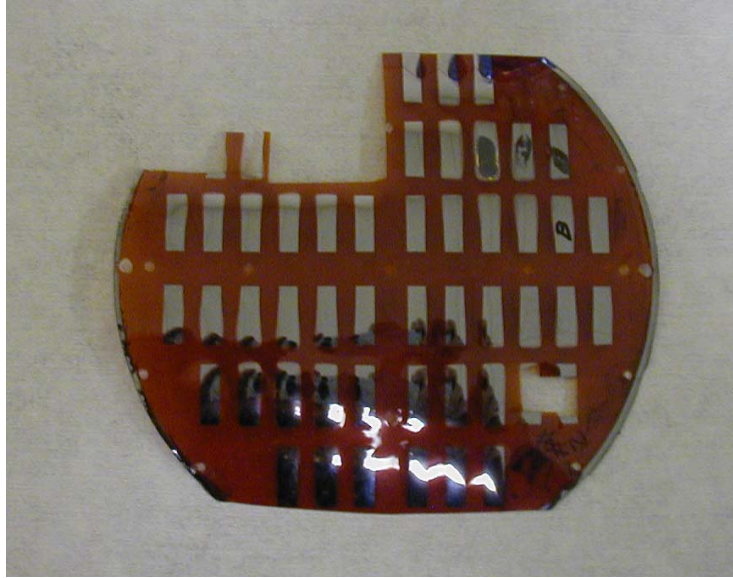


Figure 6. Typical arrangement of how samples are cut to prepare for the microscope. Si cover layer is reflective with a slight bending causing dark and light areas in several of the 1.5 cm x 0.5 cm samples.

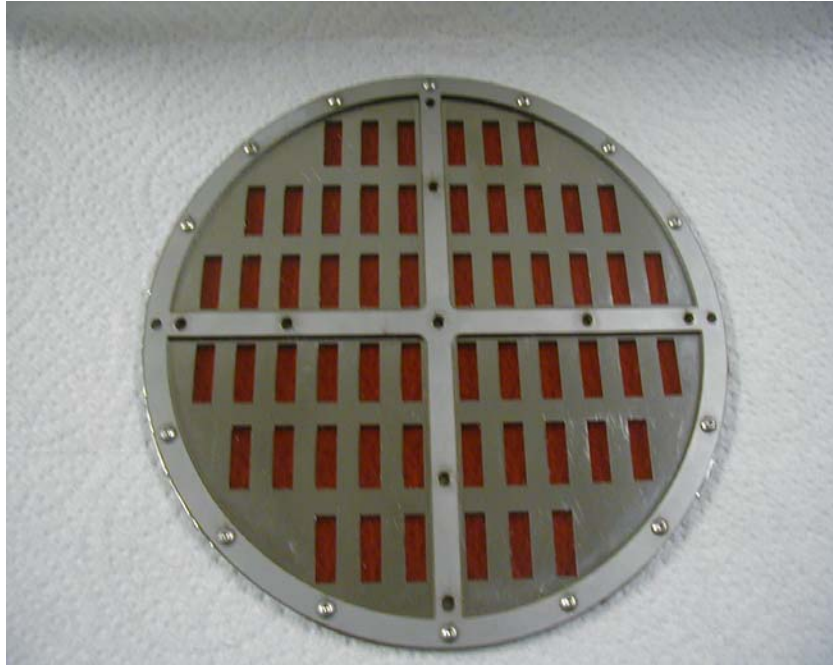


Figure 7. Sample loaded into frame and stainless steel mask.



Figure 8. Unmasked Kapton sample prepared for temperature profiling. Notice the temperature sensitive lacquer dots indicating 302 to 343EC. This data was used to set substrate at $>325^{\circ}\text{EC}$ which is needed to promote near neighbor atom ordering to provide excellent thermoelectric properties.

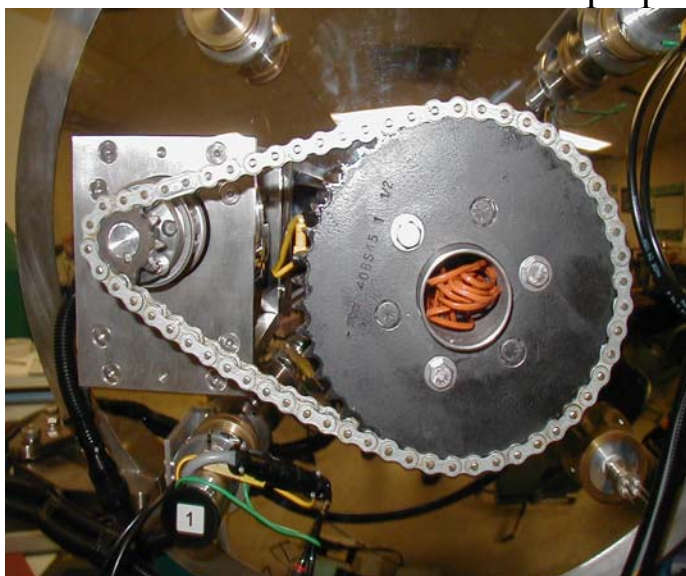


Figure 9. Chain and sprocket to adjust deposition rate.

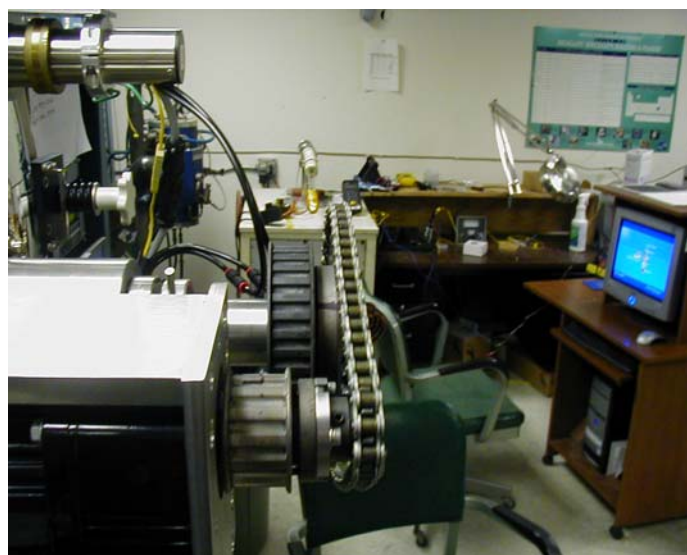


Figure 10. Side view of chain and sprocket.

From Figure 2-4, it is apparent that satisfactory film thickness has been obtained and from Figures 5-8, proper masking and temperatures have been obtained. However, for improved large area films for the project a slower deposition rate is needed. Thus, the drive train has been modified to allow for 1/8 RPM. Figures 9 and 10 show the chain and sprocket adaptations to the existing belt drive mechanism. This will allow us to return to the original drive system with very little effort.

The first temperature test was performed and it showed a Kapton temperature >302 but $<316^{\circ}\text{EC}$. Sample wheel was set at 1/8 RPM and temperature set point at 350°EC . Another test will be run with a set point of 375°EC .

4 QW Couples Fabrication with Mo Contacts on Si

An earlier single couple device that was fabricated with N-type Si/SiGe and P-type $\text{B}_4\text{C}/\text{B}_9\text{C}$, is shown in Figure 11. It also has Mo contacts. However, the substrate with the N & P legs was single crystal Si and alumina was used to electrically insulate the N and P legs. It has operated for more than 4500 hours with some degradation (shown in Figure 12). Hi-Z is investigating the cause of the failure in this couple and will report the results in the future reports. The Si single crystal substrates have a high thermal conductivity and therefore are a major heat leak. Assuming bulk thermal- ϵ for the film the ZT of the couple without the Si substrate is calculated to be ~ 4 @ 25°C . To reduce this heat loss and increase efficiency, Kapton is being pursued in place of Si since its thermal ϵ is \sim two orders of magnitude lower than Si. Kapton is also flexible, useful up to $\sim 300^{\circ}\text{C}$, and much lower in cost than 5: m thick Si. While Kapton has a higher coefficient of thermal expansion than Si/SiGe, deposition of the QWs on both sides of the Kapton helps balance out the differential thermal stresses. For temperatures above 300°C , Hi-Z is developing an inorganic materials approach that can operate at higher temperatures and minimize heat losses.

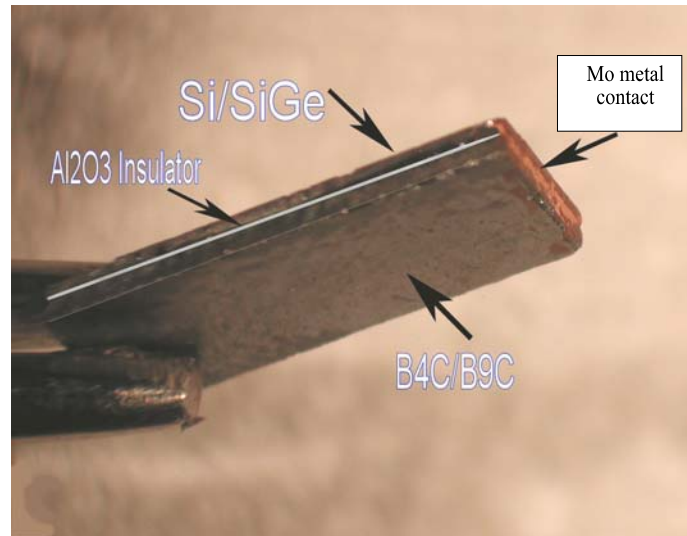


Figure 11. QW Si/SiGe- $\text{B}_4\text{C}/\text{B}_9\text{C}$ couple for thermal stability test. The Mo was deposited by an improved sputtering process to obtain a lower contact resistance. An Al_2O_3 insulator was used to electrically separate the N & P legs. The power output is within a few percent of the expected calculated values.

The latest achievement in fabricating a two couple module helps meet the goal of depositing the QW films on Kapton and then joining the N and P legs with Mo contacts. Hi-Z's other high efficiency quantum well programs will also benefit from the materials and processes developed for this couple. The next step is to define and establish acceptable quantum well fabrication variables to produce a scalable and repeatable recipe for the Navy mW sensor power supply and the Army/DOE waste heat recovery programs.

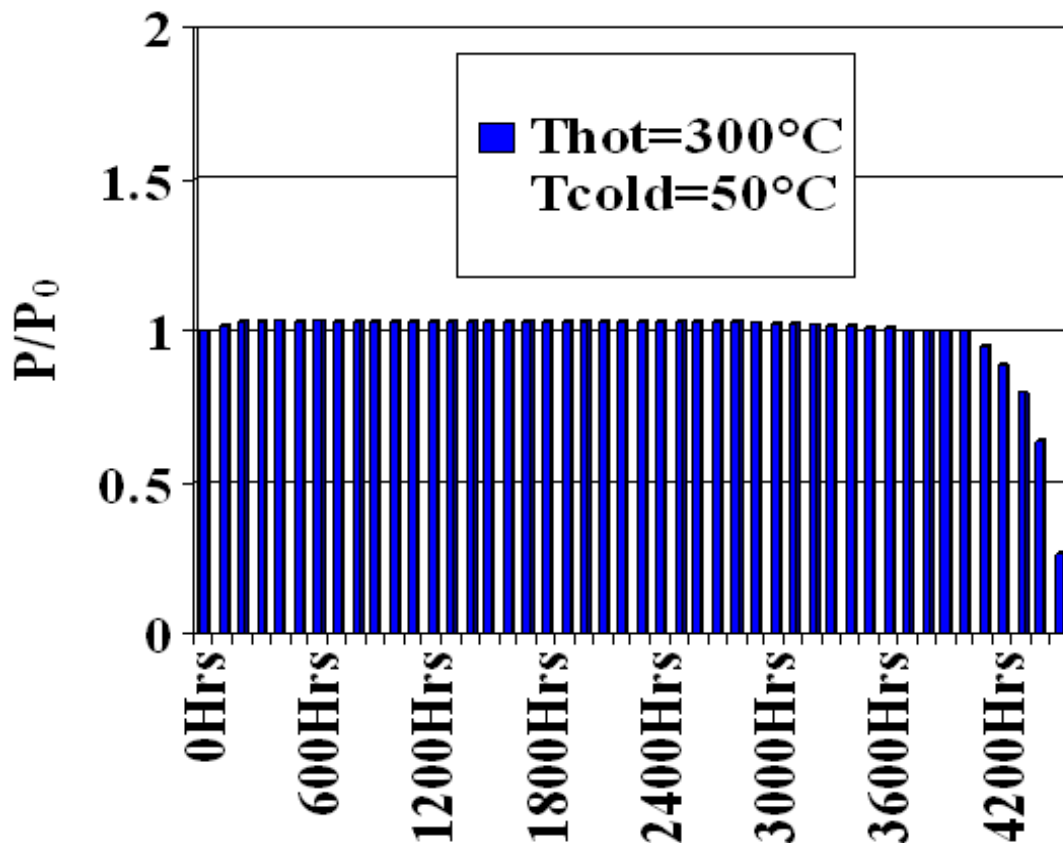


Figure 12. Power ratio life test data.

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